Synthesis and structure of grafted layer of silicas modified with alkanesulfonic acid

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A convenient method for preparation of silicas modified with alkanesulfonic acid through the reaction of $NaHSO_3$ with the C_2H_3 groups grafted on the SiO_2 surface was proposed. The influence of the carrier and the structure of the grafted layer on the modification process was studied by DRIFT, MAS NMR, and temperature-programmed desorption mass spectrometry (TPD-MS). It was found that at most 40% of the C_2H_3 groups transform to the acid sites, which mostly have the structure of 2-Si-ethanesulfonic acid. The mechanism of the thermal decomposition of the grafted groups, which are stable up to 240 °C, was proposed. The monomeric structure of the grafted layer leads to partial olygomerization of the C_2H_3 groups through the C=C bonds.

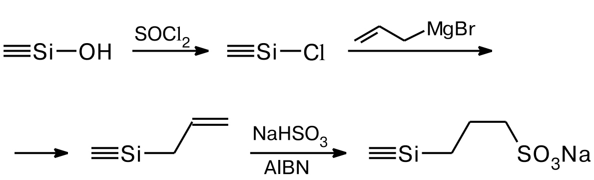
Key words: chemically modified silica, vinyl groups, sulfo groups, $NaHSO_3$, temperature-programmed desorption mass spectrometry, IR spectroscopy, NMR.

Cation-exchange resins based on organic polymers containing sulfo groups[1] are used as catalysts for a number of organic reactions. However, such materials are thermally and chemically unstable, and the most fraction of the acid sites are poorly accessible to reactants. These drawbacks can be eliminated when silicas with a derived surface are modified with organic sulfonic acids (SiO_2—SO_3H).[2—6] Grafted aliphatic sulfonic acids are of a special interest because they undergo hydrothermal desulfurization to a lesser extent than their aromatic analogs under conditions of a catalytic reaction.

Several methods for the preparation of such sulfonic acids are known. A one-step modification of the SiO_2 surface with silanes containing target groups (silanization)[7] has not been used widely because of inaccessibility of the reagents. Therefore, to prepare the sulfoalkyl silicas, reactions with organic groups preliminarily grafted on the carrier surface (*viz.*, method of "surface assembling")[2] are more often used. As a rule, the "surface assembling" is much less efficient than reactions in solution, and the conditions for the "surface assembling" differ markedly.[3—6] Nowadays, the oxidation of the grafted mercaptopropyl groups for the preparation of SiO_2—SO_3H is most extensively employed.[8,9] However, the reaction on the SiO_2 surface occurs nonselectively and at least 50% of the alkyldisulfide groups are formed along with the target SO_3H groups.[6] These groups as well as residual mercaptopropyl groups are very reactive and substantially deteriorate the ion-exchange and catalytic properties of the SiO_2—SO_3H.

Meanwhile, the addition of $NaHSO_3$ at the C=C double bonds is also well known. This reaction produces sulfonic acids in high yields.[10] The reaction was also used[11] for the preparation of sulfonic acids grafted on the silica surface (Scheme 1).

Scheme 1



Preparation of SiO_2—SO_3H according to Scheme 1 is a complicated multistage process resulting in a material with a low concentration of the grafted acidic groups, and the procedure is poorly reproducible. Data on the structure of the sulfoalkyl groups that formed on the surface as well as on the effect of the reaction conditions on the conversion are not available in the literature. The mechanism of the synthetic procedure has also not been discussed.

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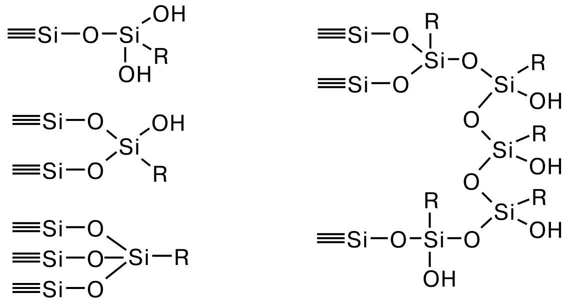
Vinylsilica (SiO_2—C_2H_3), the most available of silicas containing unsaturated groups on the surface, was chosen in our study. Earlier, it was not used for the preparation of SiO_2—SO_3H. This work was aimed at a search for the conditions for the maximal conversion in $NaHSO_3$ addition to the grafted C_2H_3 groups and a study of the chemical nature of this process. Since the structures of both silica carrier and the grafted layer can affect substantially the reaction rate and mechanism on the surface, these parameters were varied in the study.

Results and Discussion

According to the literature data,[3,4] the structure of the grafted layer on modified silicas prepared by silanization significantly depends on the presence of water in the reaction mixture. Silicas with a "monomeric" coverage are usually obtained under water-free conditions. Therefore, the silane links to SiO_2 only through the reaction with the surface silanol groups. To synthesize the modified silicas with a "polymeric" coverage, water is added to the reaction mixture. As a result, the grafted layer consists of polysiloxane fragments bound to the surface (Scheme 2).

Scheme 2



"Monomeric" coverage

"Polymeric" coverage

Table 1. Characteristics of the prepared SiO_2—C_2H_3 materials

Sample	Trade mark of silica gel	Type of coverage	$C_{C_2H_3}$ /μmol g^{-1}
1	L100/250	Monomeric	340
2	L100/250	Monomeric	290
3	L100/250	Polymeric	690
4	KSK	Monomeric	230

Samples of the SiO_2—C_2H_3 with the "monomeric" and "polymeric" grafted layers based on the Lachema silica gel (Czechia) and KSK silica gel were used as starting materials (Table 1). To prepare the SiO_2—SO_3H, these materials were treated with an aqueous solution of $NaHSO_3$ in the presence of the initiator of free-radical reactions, AIBN. The conditions for the maximal conversion of the C_2H_3 groups to sulfoalkyl groups were found by varying the initiator nature, time, and reaction temperature. The concentrations of the acidic (C_{H^+}) and residual vinyl ($C_{C_2H_3}$) groups in the materials obtained were determined (Table 2).

First of all, the effect of the initiators in the free-radical reaction of $NaHSO_3$ with the surface vinyl groups were studied. The reaction of the SiO_2—C_2H_3 with a $NaHSO_3$ solution was carried out both in the absence of the initiator (under Ar) and in the presence of initiators. As can be seen in Table 2, C_{H^+} is much lower in the material prepared without initiation (sample **5**) than in samples prepared under similar conditions in the presence of the initiators (*viz.*, AIBN (sample **6**) and oxygen (sample **7**, $T = 80$ °C)).

The formation of the grafted groups upon the interaction of $NaHSO_3$ with SiO_2—C_2H_3 can be presented by Scheme 3.

The reaction produces 1-Si- and 2-Si-ethanesulfonic acids (**A** and **B**, respectively) as well as 2,4-Si-butanesulfonic acid (**C**) or other similar surface compounds along with the products of oligomerization of the C_2H_3 groups at the C=C bond.

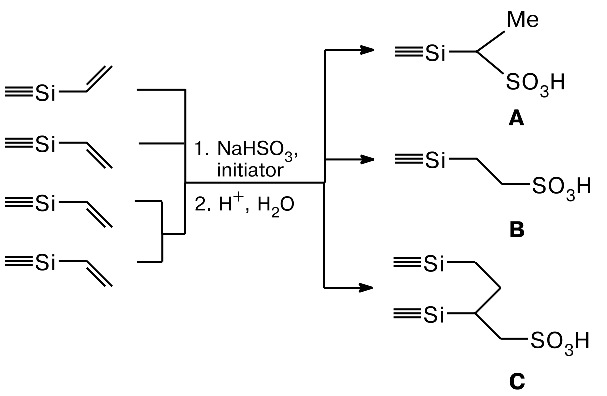
Table 2. Conditions of synthesis and the concentration of grafted groups on SiO_2—SO_3H

SiO_2—SO_3H	Initial SiO_2—C_2H_3	Conditions of synthesis of SiO_2—SO_3H		C_{H^+}	$C_{C_2H_3}$
		T/°C	t/min	/μmol g^{-1}	
5*	**1**	80	180	18	201
6**	**1**	70	840	112	139
Series **7**	**1**	23—95	180	83—129	59—114
Series **8**	**2**	80	15—240	35—102	103—160
Series **9**	**3**	80	15—360	48—235	302—590
Series **10**	**4**	20	25—360	0—10	63—147
Series **11**	**4**	85	20—360	32—62	42—132

* Initiator was absent; synthesis was performed in argon atmosphere.

** Initiation by AIBN in a 10% $Na_2S_2O_5$ solution in H_2O—MeOH (1 : 1).

Scheme 3



It was found that the difference between $C_{C_2H_3}$ in the starting SiO_2—C_2H_3 and $C_X = C_{H^+} + C_{C_2H_3}$ in SiO_2—SO_3H was greater than zero in all the prepared materials. Hence, either a fraction of the C_2H_3 groups was removed from the silica surface during modification or other fragments, for example, **C**, were formed along with the target products of $NaHSO_3$ addition to the C_2H_3 group in a 1 : 1 ratio (**A** and **B**, see Scheme 3). Hence, we compared the conversion of the C_2H_3 to sulfoalkyl groups with the $C_{C_2H_3}$ value in the starting material (ω_{H^+}); the $\omega_{C_2H_3}$ and ω_X values were similarly calculated.

It was found that the maximal value of ω_{H^+} is 30—40% for all the SiO_2—C_2H_3 samples, when both the temperature (Fig. 1) and the time of synthesis (Fig. 2) increased irrespectively of the silica template and the structure of the grafted layer. The concentration $C_{C_2H_3}$ decreases but does not reach zero (see Table 2). Incomplete transformation of the grafted groups has often been found[3—6] in the surface assembling reactions, and this fact was usually explained by the inaccessibility of these groups. A similar explanation seems also to be valid in our case. After modification of silica with the C_2H_3 groups, its surface becomes hydrophobic, *i.e.*, the water wetting angle increases. Since treatment with $NaHSO_3$ was performed in an aqueous solution, a fraction of the C_2H_3 groups in the silica pores is inaccessible for the reaction because of capillar effects. This factor can be one of the reasons for the retardation of the reaction of $NaHSO_3$ with the SiO_2—C_2H_3 in the "polymeric" grafted layer compared to the reaction with SiO_2—C_2H_3 in the "monomeric" coverage (*cf.* Fig. 2, series **8** and **9**).

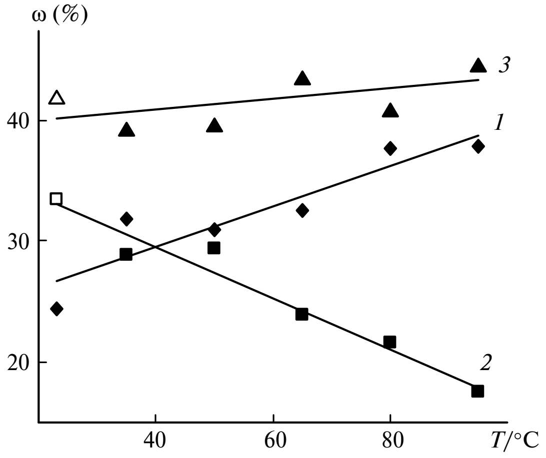


Fig. 1. Plot of ω_{H^+} (*1*), $\omega_{C_2H_3}$ (*2*), and ω_X (*3*) *vs.* temperature of synthesis for SiO_2—SO_3H, series **7**.

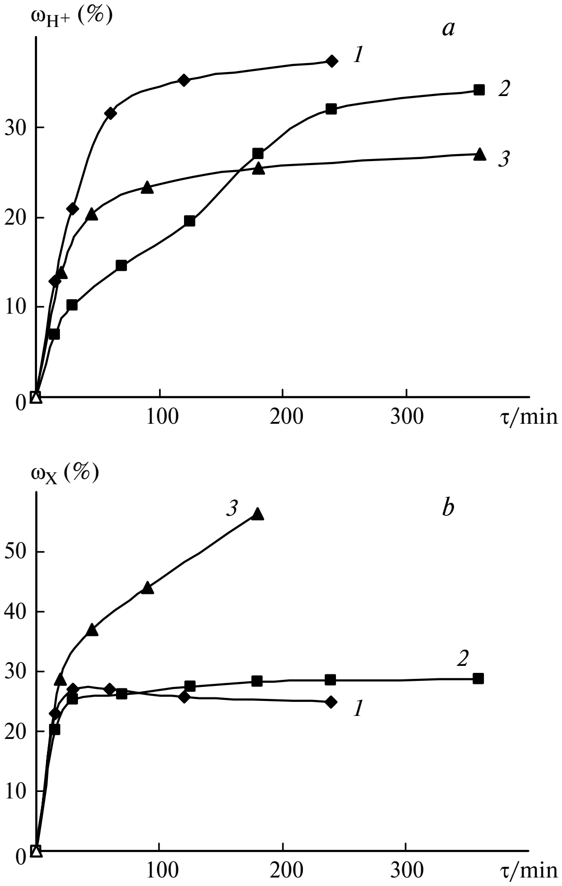


Fig. 2. Plot of ω_{H^+} (*a*) and ω_X (*b*) *vs.* time of synthesis for SiO_2—SO_3H, series **8** (*1*), **9** (*2*), and **11** (*3*).

In spite of the fact that the structural parameters of the silicas used were close and the pore sizes were much greater than the molecule diameter, it was found that the carrier nature substantially affect $NaHSO_3$ addition. An increase in the temperature of synthesis for the material based on the Lachema silica gel only slightly increases ω_{H^+} (see Fig. 1), whereas the composition of the surface groups on the KSK silica gel changes completely (see Table 2, series **10** and **11**). For the SiO_2—SO_3H based on the Lachema silica gel, ω_X rapidly reaches a constant value, which is independent of the synthesis conditions and the structure of the grafted layer. For materials based on the KSK, ω_X continuously increases in time (see Fig. 2).

A probable reason for the differences found is a low hydrolytic stability of the surface of the KSK template. Fast increase in ω_X at the onset of $SiO_2—C_2H_3$ treatment with a $NaHSO_3$ solution can be due to the desorption of polysiloxane fragments physically adsorbed on the surface and to the oligomerization of the C_2H_3 groups at the C=C bonds. After these processes were completed, ω_X for the materials based on the Lachema silica gel reached a constant value and that for KSK continued to increase because of decomposition of the template surface layer. A noticeable decrease in $C_{C_2H_3}$ at an extremely low C_{H^+} for materials of series **10** (see Table 2) can be explained by the lower rate of the formation of the acidic groups compared to the rate of hydrolysis of the sections of the KSK surface, which became hydrophilic due to modification. Another possible reason for the carrier effect on the reaction is a difference in the mechanism of interaction between the $SiO_2—C_2H_3$ and $NaHSO_3$ on various carriers.

To verify this suggestion and to study in detail the composition of the grafted layer, the $SiO_2—SO_3H$ synthesized were studied by DRIFT, MAS NMR, and temperature-programmed desorption mass spectrometry (TPD-MS).

In the DRIFT spectrum of $SiO_2—C_2H_3$ (sample **3**, see Table 1), the absorption bands ν(C—H) at 3070, 3030, 2992, and 2965 cm^{-1} and δ(C=C) at 1605 cm^{-1} similar to those in the spectrum of $Cl_3SiC_2H_3$ are observed. The intensities of these absorption bands in the spectrum of $SiO_2—SO_3H$ (series **9**, τ = 360 min) decrease and the absorption bands ν(C—H) at 2973, 2930, 2912, and 2872 cm^{-1} appear, indicating the addition of $NaHSO_3$. The absorption band at 2930 cm^{-1} can be assigned to the $\nu_{as}(CH_2)$ vibrations of 2-Si-ethanesulfonic acid.[12]

In the ^1H MAS NMR spectra of all the silicas, an intense signal is observed in the 1.9—2.3 ppm region, which is due to superposition of the peaks of both isolated (1.7 ppm) and vicinal (2.4 ppm) Si—OH groups as well as of the hydrogen-bound water molecules (3.6 ppm).[6] The signal at 5.9 ppm from the C_2H_3 groups is present in the spectrum of $SiO_2—C_2H_3$ (sample **3**). In the spectrum of $SiO_2—SO_3H$ (series **9**, τ = 360 min), the intensity of this signal decreases and two shoulders (1 and 3 ppm) appear on the multicomponent signal at 2.1 ppm, which are most likely due to the $C\underline{H}_2—Si$ and $C\underline{H}_2—SO_3H$ fragments, respectively, of 2-Si-ethanesulfonic acid.

As expected, signals of the carbon atoms of the grafted C_2H_3 groups, $CH_2{=}\underline{C}H—Si$ (129 ppm) and $\underline{C}H_2{=}CH—Si$ (136 ppm), are found in the ^{13}C MAS NMR spectrum of $SiO_2—C_2H_3$ (Fig. 4). These signals are also present in the spectrum of $SiO_2—SO_3H$ (see Fig. 3), and new signals from the fragments of 2-Si-ethanesulfonic acid: $\underline{C}H_2—Si$ (7 ppm) and $\underline{C}H_2—SO_3H$ (47 ppm) appear. In addition, a signal is seen in the region typical of the aliphatic carbon atoms not bound to heteroatoms[12] (23 ppm). This signal can be assigned to the Me groups in the **A** or $C—\underline{C}H_2—C$ groups in **C** (see Scheme 3). The rest weak peaks in the spectrum are rotatory satellites of the signals.

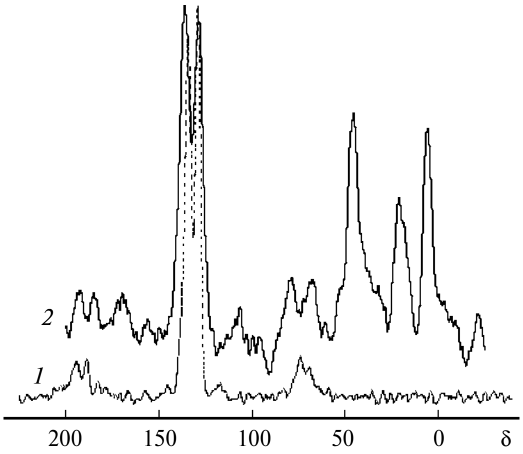


Fig. 3. ^{13}C MAS NMR spectra: *1*, $SiO_2—C_2H_3$ (sample **3**), *2*, $SiO_2—SO_3H$ (series **9**, τ = 360 min).

The TPD-MS technique[13—15] was very informative in studies of modified silicas. This method allowed us not

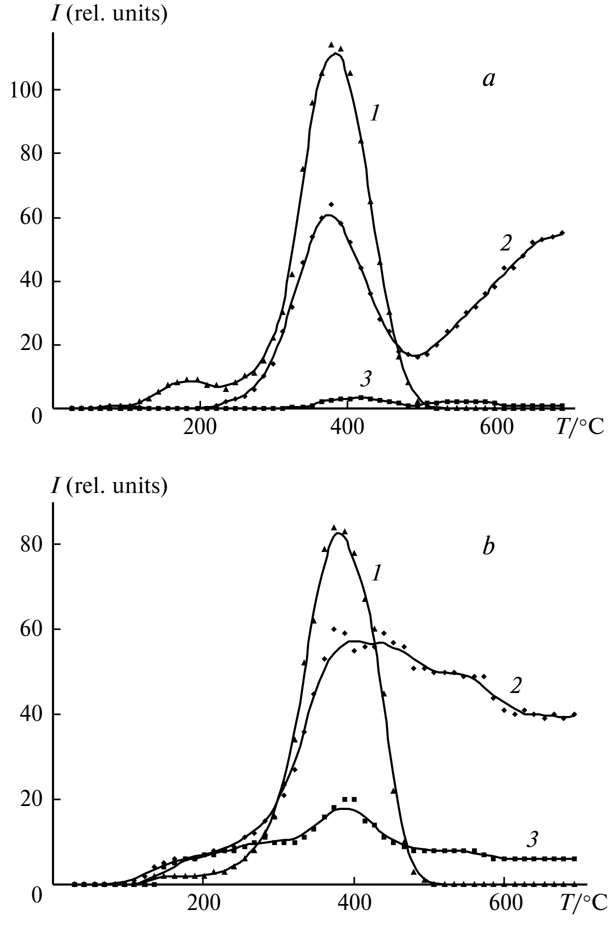
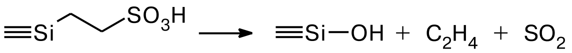


Fig. 4. Thermal decomposition of "polymeric" $SiO_2—SO_3H$ (series **9**, τ = 360 min) (*a*) and "monomeric" $SiO_2—SO_3H$ (series **8**, τ = 240 min) (*b*): *1*, SO_2, *2*, C_2H_4, *3*, C_3H_6.

only to determine the limits of the thermal stability of the material, which are important for its application in catalysis, but also to reveal the structure of the grafted layer. This method showed that the thermal decomposition of the "polymeric" SiO_2—SO_3H (series **9**, τ = 360 min) is characterized by SO_2 evolution with the maximal intensities at 175 and 375 °C (Fig. 4). Two processes of the SiO_2—SO_3H thermal destruction indicate the simultaneous occurrence of the grafted sulfoalkyl groups with different structures. A comparison of the peak areas with the curve for SO_2 evolution (see Fig. 4) shows that a less stable species of sulfonic acid comprises ~7% and more stable species is 93% of the total groups, whose decomposition evolves SO_2. A comparison of these findings with the IR-spectroscopic and NMR data allows the assignment of the low-temperature process to the decomposition of the grafted 1-Si-ethanesulfonic acid, whereas the high-temperature process can be attributed to decomposition of 2-Si-ethanesulfonic acid (**A** and **B**, respectively, see Scheme 3). The maximum of ethylene evolution from SiO_2—SO_3H (series **9**, τ = 360 min) coincides with the high-temperature maximum of SO_2 evolution. Therefore, the decomposition of 2-Si-ethanesulfonic acid that is stable up to 240 °C can be presented by Scheme 4.

Scheme 4



The evolution of ethylene and SO_2 during thermal decomposition of the "monomeric" SiO_2—SO_3H occurs in the same temperature range as that of the "polymeric" SiO_2—SO_3H (see Fig. 4). However, the peaks of C_3 and C_4 alkenes appear in the mass spectra of the products of thermal destruction of the "monomeric" SiO_2—SO_3H, and these peaks were not found in the spectra of the "polymeric" sample. The profile of thermal evolution of these products has a maximum at 385 °C, which coincides with the maximum of SO_2 evolution. The appearance of C_3 and C_4 alkenes in the products of the thermal decomposition of the "monomeric" SiO_2—SO_3H is due to the presence of the fragments of 2,4-Si-butanesulfonic acid on the surface (see Scheme 3) or other similar compounds, which are the products of oligomerization of the grafted C_2H_3 groups. The intensity ratios for the peaks of C_3 and C_4 alkenes to the peak of ethylene are the same for the SiO_2—SO_3H based on both the Lachema (series **8**, τ = 240 min) and KSK (series **11**, τ = 360 min) silica gels. This fact points to the close ratio between the C_2 and oligomeric grafted groups in these materials and, hence, the close compositions of the grafted layers.

The trend of the C_2H_3 groups in the "monomeric" grafted layer to oligomerization to produce carbon chains can be rationalized as follows. The silane bonding with the surface Si—OH groups in the synthesis of the "monomeric" coverage produces a spatially ordered system of the C_2H_3 groups directed to one side from the surface, which are accessible to oligomerization through the double bonds. The C_2H_3 groups in the "polymeric" grafted layer are spatially disordered, and their rotation around the polysiloxane chains is impossible (see Scheme 1). Therefore, the probability of such an arrangement of the neighboring C_2H_3 groups in the "polymeric" layer at which oligomerization is possible is substantially lower than that in the "monomeric" layer. As a result, oligomerization is supressed.

Hence, when the SiO_2—C_2H_3 interacts with an $NaHSO_3$ aqueous solution, at least 40% C_2H_3 groups are transformed to the sulfoalkyl groups, mainly with the 2-Si-ethanesulfonic acid structure (**B**, see Scheme 3), which are stable up to 240 °C. A fraction of the C_2H_3 groups does not react because of capillar effects. A decrease in the overall concentration of the acidic and C_2H_3 groups in the SiO_2—SO_3H compared to $C_{C_2H_3}$ in the starting SiO_2—C_2H_3 is due to oligomerization of the C_2H_3 groups through the C=C bonds, which is typical of materials with the "monomeric" grafted layer only, as well as to the destruction of the grafted layer. The differences found between the Lachema and KSK silica gels are likely due to the lower hydrolytic stability of the latter carrier.

Experimental

The DRIFT spectra were recorded against KBr on a Bruker Vector 22 spectrometer supplied with a Harrick Scientific Praying Mantis attachment. Before recording the spectra, samples were heated in a vacuum in the cell up to 130 °C for 1 h, and the spectrum was recorded after cooling to room temperature.

The ^1H MAS NMR spectra were obtained on a Bruker MSL-400 instrument (400 MHz, rotation frequency 8—12 kHz). Before recording the spectra, samples were stored for 15 h at 110 °C and 0.01 Pa in NMR ampules, and then the ampules were sealed. The ^{13}C MAS CP (cross-polarization) NMR spectra were recorded on a Varian UNITY/nova-300 instrument (300 MHz; rotation frequence 4 kHz; contact time 1 ms); the air-dry samples were used.

The TPD-MS studies were carried out by heating samples in a high vacuum ($< 10^{-3}$ Pa) at a heating rate of 9 deg min^{-1}. The products evolved were analyzed on a MKh-7304A mass spectrometer.

The concentration of acidic groups in the prepared materials was determined by potentiometry at ~20 °C. A 0.05 *M* solution of KCl (25 mL) was added to a weighed portion of silica (0.2—0.5 g), and the suspension was titrated with stirring by an alkali solution. The pH values were measured with an accuracy of ±0.01 after equilibration, *i.e.*, after changes in pH was less than the measurement accuracy, on an EV-74 Ionomer with glass ELS-41 and silver chloride electrodes. The concentration of the acidic groups was calculated by the Gran method.

The concentration of the C_2H_3 groups was estimated by bromatometric titration. A weighed portion of the material (0.4 g) was stored in a closed flask with a Br_2 solution prepared from a specified volume of the standard solutions of $KBrO_3$, NaBr, and H_2SO_4. Then to the solution KI was added, which reacted with excess Br_2, and I_2 that formed was titrated with a $Na_2S_2O_3$ solution.

The silica gels L100/250 (Lachema, Czechia, 310 m^2 g^{-1}, d_{por} = 6 nm) and KSK (Russia, 165 m^2 g^{-1}, d_{por} = 22 nm) were used as starting carriers.

Before silanization, silica gel was refluxed in conc. HNO_3 for 5 h, washed with water, dried, and calcined for 8 h at 550 °C. Then silica gel was heated with distilled trichlorovinylsilane (1 mmol g^{-1} SiO_2) in a water-free organic solvent[12] (samples **2** and **3** in toluene at 100 °C; samples **1** and **4** in *o*-xylene at 135 °C) for 8 h. To prepare sample **3** (polysiloxane coverage), water (1 mmol g^{-1} SiO_2) and pyridine (reagent grade, 5 mmol g^{-1} SiO_2) were added to the reaction mixture. Then the sample was washed several times with the same solvent, in which the synthesis was performed, and with Me_2CO dried above K_2CO_3 in the Soxhlet apparatus, then several times with water, and dried succesively in air and in a vacuum at 120 °C.

Addition of $NaHSO_3$ to the SiO_2—C_2H_3 was carried out in an aqueous solution (20% $Na_2S_2O_5$ solution), a portion of $Na_2S_2O_5$ was equal to that of the SiO_2—C_2H_3, *i.e.*, $Na_2S_2O_5$ was in a 20—50-fold excess relative to the C_2H_3 groups. Sample **5** was prepared in an Ar atmosphere. Sample **6** was synthesized in the presence of AIBN (0.1 mmol g^{-1} SiO_2). During the synthesis of all the rest SiO_2—SO_3H samples, air was bubbled through the reaction mixture. After reaction, the samples were washed with water from excess $NaHSO_3$, then with a 10% HCl or HNO_3 solutions, and finally with deionized water until the washing solutions were neutral.

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